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COUNTRY	USSR	DATE DISTR.	28 May 1948
SUBJECT	Chemistry	NO. OF PAGES	13
PLACE ACQUIRED	USSR	NO. OF ENCLS. (LISTED BELOW)	
DATE OF INFORMATION	1947	SUPPLEMENT TO REPORT NO.	

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SOURCE Russian periodical, Zhurnal Fizicheskoy Khimii, Vol XXI, No 3, 1947. (FDB per Abs 2T47 — Translation specifically requested.)

INORGANIC PEROXIDES

XI. THE HIGHER OXIDES OF POTASSIUM

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[Note: A list of previous works of the Laboratory of Inorganic Peroxides is appended. Numbers in parentheses refer to the bibliography.]

Until a short time ago the existence of the following oxides of potassium were accepted: K_2O, K_2O_2, K_2O_3, K_2O_4. In recent years, opinions on the nature of higher oxides of potassium have radically changed. Study of the roentgen structure and magnetic properties of potassium tetroxide led to a formula of KO_2 with an ion O_2^-, which was known up till now only in a free condition in electrical discharges in oxygen and in the phenomena of thermionic emission. In the short article which we published in 1938, we showed by tensimetric measurements that the potassium trioxide K_2O_3, which is described by many authors, is not a separate substance but is a mixture of KO_2 and K_2O_2 (1). This deduction was subsequently confirmed by other methods. Consequently, there exist only three oxides of potassium, K_2O, K_2O_2, and KO_2. In the present work a more complete account of these studies is given and the thermochemistry of oxides of potassium is reexamined on the basis of the data received.

After the works of Gay-Lussac and Thenard, Harcourt, Joannis, Forcrand, Rengade, Kraus and Whyte, and others, the existence of four oxides of potassium was considered accepted: K_2O, K_2O2, K_2O_3, and K_2O_4. However, until a short time ago the structure of these oxides had been studied very little.

Zintl, Harder, and Dauth (2) found that potassium oxide K_2O has an antifluorite lattice and is constructed out of ions K^+ and O^{--}. Apparently potassium peroxide contains an ion O_2^{--}, the structure of which was explained in the study of the roentgen structure of BaO_2 and SrO_2(3). Roentgenographic study of the higher oxide of potassium, potassium tetroxide, which was

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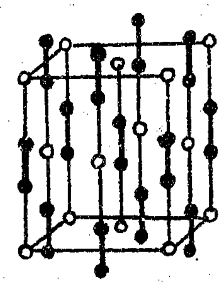
conducted in our laboratory by Kasatochkin and Kotov (4), led to the structure $K^+O_2^-$ with an ion O_2^-, in agreement with the magnetic properties of this oxide (5). According to the Debye and Scheurer method, a tetragonal lattice with centered faces of a calcium carbide type was established. The dimensions of the elementary nucleus are: a = 5.70 Å, c = 6.72 Å, c/a = 1.178; and it contains 4 molecules KO_2. The density of 2.15, which is calculated from the dimensions of the nucleus, agrees with the pycnometric density of 2.158 (see below). Comparison of the calculated intensities of the line with the observed intensities gave d_{O-O} = 1.28 Å for the distance between the two closest oxygen atoms. The discovered structure of the lattice of potassium tetraoxide is completely analogous to the structure of strontium peroxide and barium peroxide, and is a lattice of rock salt, lengthened in one direction because of the form of the ion O_2^- (Figure 1).

Helms and Klemm (6) found an analogous structure for RbO_2 and CsO_2. All of these oxides have a tetragonal lattice; their parameters are presented in Table 1.

The ion O_2^- in these lattices can be looked upon as a revolving ellipsoid with the length of the large semiaxis 2.02 Å and the small semiaxis 1.51 Å.



ion O_2^- o ion K^+

Table 1

Oxide	A	C	C/A	d Pyconometric	d Roentgenographic
KO_2	5.70	6.72	1.178	2.158	2.15
RbO_2	6.00	7.03	1.172	3.06	3.06
CsO_2	6.28	7.24	1.153	3.80	3.80

The higher oxides KO_2, RbO_2, and CsO_2 are yellow and have paramagnetism corresponding to one unconnected electron, (oxides of alkali metals with a composition of M_2O and M_2O_2 are colorless and diamagnetic). Apparently the carrier of these properties is the ion O_2^-, which according to Pauling has the structure :O $\overset{...}{—}$ O: with one ordinary and one three-electron bond (^2P-condition). In the terms of the method of molecular orbits the possible structure of the O_2^- ion is KK $(zo)^2(yo)^2(xo)^2(w\,\pi)^4(v\,\pi)^3$ 2Pg with three (surplus) connecting electrons. The energy of bond in the ion O_2^- must, consequently, make up approximately three-fourths of the energy of bond in the molecule O_2, which has four connecting electrons. For the heat of reaction $O + O^- = O_2^-$, ~86 kcal was found — a value close to 0.75 D_{O_2} (88 kcal). This ion, which was unknown in chemistry until a short time ago, seemed the most stable of all oxygen ions (7).

In a free condition, the ion O_2^- had already been discovered in electrical discharges in oxygen and phenomena of thermionic emission. In tests with thermionic emission from barium oxide, it was found that with 800 degrees, electrons and negative ions are emitted simultaneously. With the aid of a mass spectrograph it was established that these negative ions have the composition O_2^- (8).

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Consequently, the higher oxides of potassium rubidium, and cesium would more correctly be called "dioxides."

With regard to potassium trioxide, it was not clear whether the preparations described by various authors were separate substances or were a mechanical mixture of KO_2 and K_2O_2, corresponding to the composition K_2O_3.

In 1811, Gay-Lussac and Thenard (9) showed that in combustion of potassium by oxygen, and oxide similar in composition to K_2O_3 is obtained. However, Harcourt (10), having established the composition of higher oxides of potassium in his classic work in 1862, emphasized that in oxidation of metallic potassium by oxygen it is impossible to obtain intermediate products of oxidation between K_2O_2 and K_2O_4. In 1894, Holt and Sims (11), repeating the tests of Harcourt, also failed to obtain potassium trioxide. Erdman and Koethner (12) in studying the higher oxides of rubidium did not discover a trioxide of this metal. Later, Kraus and Whyte (13), in oxidation by oxygen of metallic potassium in liquid ammonia, also observed only the formation of tetraoxide and peroxide of potassium.

Moreover, a number of authors maintain that in thermal disintegration of K_2O_4 or in incomplete oxidation of K_2O_2, potassium trioxide is obtained. The approximate correspondence of the composition of the obtained compounds to the formula K_2O_3 and their darker color, distinguishing them from yellow potassium tetraoxide and colorless potassium peroxide, are produced as a supporting argument.

However, neither argument is conclusive. Both in thermal disintegration of KO_2 and in oxidation of K_2O_2 it is possible to obtain a preparation of any composition within the limits of K_2O_2 to $KO_2(K_2O_4)$ depending upon the duration of the reaction. Even the color of the proposed potassium trioxide differs, with different authors, from yellow to black, which, apparently, is because of the mixture.

Tensimetric measurements with tetraoxide of potassium and products of its thermal disintegration are one of the methods which can be used to clear up the question of the existence of potassium trioxide. In the case of formation of intermediate phases corresponding to potassium trioxide, the characteristic graduated curve would have to be observed.

The measurement of the dissociation pressure was made by Forcrand (14), Kraus and Whyte (13), and Centnerszwer and Blumenthal (15). However, their results differ greatly. According to Forcrand, potassium tetraoxide at 385 degrees has a hardly noticeable dissociation pressure, while at the same time Centnerszwer and Blumenthal found for this same temperature P_{O_2} = 240 mm Hg. Kraus and Whyte give for 300 degrees the value of 0.17 mm Hg. Consequently, it is impossible to make any deductions from the measurements of these authors, as it remains unclear which value corresponds to equilibrium.

The existence of potassium trioxide seems doubtful to us also in comparing the possible structure of this substance with properties ascribed to it. Of the possible structures of the ion O_3^-,

$$\underset{\text{I}}{:\ddot{\underset{..}{O}}:\ddot{\underset{..}{O}}:\ddot{\underset{..}{O}}:^{--}} \qquad \underset{\text{II}}{O^- \; {}^-\ldots} \underset{\text{III}}{O_2^- \; {}^-}\ldots O$$

the first is eliminated, as such an ion would have to be colorless and diamagnetic, while at the same time the preparations described up till now are composed of K_2O_3, are colored and, as Helms and Klemm found, are paramagnetic.

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However, structures II and III, where the bond is accomplished by polarizing and dispersion forces, are hardly compatible with thermal stability of the preparations of a composition of K_2O_3.

For an explanation of these contradictions, we undertook to measure the dissociation pressure of potassium dioxide KO_2 and the products of its thermal disintegration, as well as to determine the density and refraction of KO_2, K_2O_2 and preparations of a composition of K_2O_3.

It appeared probable that the unsatisfactory results of measurements of dissociation pressure of higher oxides of potassium made by a number of authors are explained by the great sensitivity of these substances to moisture and the unsatisfactory experimental methods used. Therefore, we used an apparatus and method which allowed us to make the measurements in conditions which eliminate the possibility of decomposition of the studied preparations as a result of moisture. This apparatus and method of work are described in the following statement (17).

EXPERIMENTAL PART

Obtaining Pure Preparations of KO_2 and K_2O_2

Obtaining pure KO_2 presents some difficulties. The two known methods are the oxidation of metallic potassium with oxygen in heating and the oxidation with oxygen of potassium solutions in liquid ammonia. The first method, developed by Harcourt, produced preparations containing 90-95 percent KO_2 (10, 18). According to the second method, oxidation in liquid ammonia, 95-98 percent preparations of KO_2 were obtained (19, 6).

We chose the Harcourt method, and after altering it somewhat, obtained preparations containing 99.0-99.7 percent KO_2.

Oxidation of potassium was carried out in a vertical tube of Jena glass (with a diameter of 7 cm and a height of 30 cm), sealed at one end and supplied with a rubber stopper (in using glass, partial sticking of the latter was observed as a result of gathering dispersed dust in the first stage of oxidation). A short tube is inserted in the stopper with another tube running through it which serves as a casing for thermocouples and at the same time makes it possible to stir the reaction mixture. The two tubes are joined with a thick-walled rubber tube. The apparatus is supplied with a mercuric manometer.

The air and oxygen supplied to the apparatus was cleaned by passing through concentrated sulphuric acid, soda lime, and calcium chloride. The test showed that in more intensive drying (phosphorous anhydride and liquid air) the oxidation of potassium is not observed.

Metallic potassium which was taken for oxidation (Kal'baum) was filtered in a special apparatus at a temperature of 90 degrees through a copper mesh and a glass capillary in a current of dry nitrogen. The container with the filtered potassium was broken under dehydrated petroleum ether. The potassium was cleaned from the glass and carried in the current of nitrogen to the tube for oxidation. The remainder of the petroleum ether was pumped out with an oil pump at a temperature of 85 degrees. The charge of the metallic potassium was from 15 to 60 g.

In the first stage, oxidation was carried out with the air by heating up to 180 degrees, approximately to the composition of K_2O_2 (which was determined

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by the weight of the tube with the reaction mixture). The speed of air flow was gradually increased from 100 to 250 cm^3/min.

Further oxidation was continued with a mixture of oxygen and nitrogen with a gradual increase of the partial pressure of the oxygen from 150 mm to atmospheric pressure and with temperatures up to 370 degrees (at 380 degrees the potassium dioxide melts and oxidation is sharply retarded).

In the 15-g mass of potassium the duration of oxidation with air was 6 hours, and with oxygen and a gradual increase of the temperature to 370 degrees an additional 6 hours were required.

Further oxidation at 370 degrees until a constant weight was reached required 10 hours more. After cooling the oxygen in the atmosphere, the product, which is easily separated from the walls, was quickly discharged in the current of oxygen into the jar with the ground glass stopper and protective ground cover. It was then kept in a desiccator over phosphorous anhydride. The product is a friable bright yellow mass with a content of KO_2 of 99-99.7 percent. Harcourt carried on oxidation in a temperature up to 300 degrees and obtained preparations containing 92-95 percent KO_2.

The content of active oxygen was determined volumetrically by decomposition of potassium dioxide with water in the presence of platinum black in a special apparatus. The determination of potassium was made by titration with 0.1 N H_2SO_4.

In Table 2, data of the analysis of several specimens of KO_2 are presented.

Table 2

No	Active Oxygen Found	Active Oxygen Calculated	Content of K_2O (in percent) Found	Content of K_2O (in percent) Calculated	Content of KO_2 (in percent)
1	33.64	33.76	66.13	66.24	99.67
2	33.50		66.20		99.25
3	33.42		66.34		99.00
4	33.96		66.02		99.42

Potassium peroxide (K_2O_2) was obtained from dioxide by thermal decomposition in a vacuum of 3-4 mm Hg at 450-470 degrees for 3 hours.

The product contained 14.55-14.60 percent active oxygen (calculated 14.52 percent) which corresponds to 99.5-99.9 percent K_2O_2.

Preparations of a composition of K_2O_3 were obtained in analogous conditions, but with shorter duration of heating. After heating for one hour the reaction tube was weighed; if the oxygen content in the product was too high, the product was subjected to further decomposition for 10-15 minutes, again weighed, etc., until it reached the necessary weight. In this, no stopping nor substantial delay of the disintegration in the composition of K_2O_3 was observed. In a number of cases preparations were obtained with oxygen content lower than K_2O_3, and were rejected.

Products with a composition close to K_2O_3 ($K_2O_{2.98}$, $K_2O_{3.02}$, $K_2O_{3.06}$) were a molten mass with a yellow color somewhat lighter than tetroxide of potassium.

The obtained preparations of KO_2 were used to measure dissociation pressure, density, and refraction. The density and refraction of the preparations of K_2O_2 and K_2O_3 were also measured.

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Measurements of Dissociation Pressure of Potassium Dioxide KO_2 and Products of Its Thermal Disintegration

Tensimetric measurements would have to show whether or not the thermal disintegration of KO_2 is according to method (1) with the formation of an intermediate phase of the composition of K_2O_3, or according to method (2):

$$\left.\begin{array}{l} 2KO_2 \longrightarrow K_2O_3 + \tfrac{1}{2}O_2, \\ K_2O_3 \longrightarrow K_2O_2 + \tfrac{1}{2}O_2, \end{array}\right\} \qquad (1)$$

$$2KO_2 \longrightarrow K_2O_2 + O_2 \qquad (2)$$

In the first case the curve of dissociation pressure would have to have two stages, one with a composition of K_2O_3 and the second with a composition of K_2O_2. In the second case a horizontal course must be observed from the composition of KO_2 to K_2O_2 and a step at a composition of approximately K_2O_2 (in the absence of hard solutions). An apparatus described in the following statement, consisting basically of McBain centrifuges, a McLeod gage and high vacuum equipment, was used to measure the dissociation pressure (17). Measurements were made at three temperatures: 300, 360, and 370 degrees C. These temperatures are lower than the melting point of KO_2 (380 degrees), which eliminates the possibility of the formation of a liquid phase with a variable composition.

Constancy in time and the attainment of the same value both in separation and addition of oxygen served as criteria of which measured values were equilibrium values.

Table 3

Composition	Dissociation Pressure at 360 degrees (in mm Hg)	
	In Separating Oxygen	In Adding Oxygen
$K_2O_{3.97}$	-	1.55
$K_2O_{3.73}$	1.48	1.56
$K_2O_{3.62}$	1.43	1.58
$K_2O_{3.55}$	1.43	1.53
$K_2O_{3.47}$	1.45	1.54
$K_2O_{3.37}$	1.41	1.52
$K_2O_{3.25}$	1.35	1.40
$K_2O_{3.16}$	1.43	1.56
$K_2O_{3.09}$	1.40	1.45
$K_2O_{2.95}$	1.45	1.54
$K_2O_{2.87}$	1.37	1.43
$K_2O_{2.53}$	1.35	1.45
$K_2O_{2.30}$	1.40	1.50

The equilibrium values were reached, as a rule, after 10-15 minutes.

Table 3 illustrates the degree of agreement of the values which were obtained by separation and addition of oxygen. The divergence does not exceed the error of measurement (see below).

The gradual thermal decomposition of potassium dioxide was achieved by heating in a vacuum up to 0.01 mm Hg at a temperature of the measurements with simultaneous observation of the composition of the hard phase according

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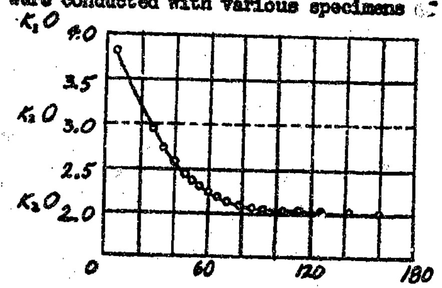
to the McBain centrifuges. Upon attaining the composition of K_2O_2 or lower, measurements with the same preparations were repeated. For this purpose purified oxygen was introduced into the apparatus, bringing the pressure up to atmospheric. After the expiration of 40-50 minutes the preparation is oxidized to the elementary composition KO_2. Each test had three cycles of measurement which gave reproducible results. During such an experiment, lasting approximately 18 hours, 20 measurements were taken. A total of 15 experiments were conducted with various specimens of KO_2.



Time in Minutes

Figure 2

In Figure 2 are presented the results of the measurement of the speed of thermal disintegration of KO_2 at 360 degrees and a vacuum up to 0.1 mm Hg. The kinetic curve has a smooth course and a kink is not observed at the point corresponding to the composition of K_2O_3.

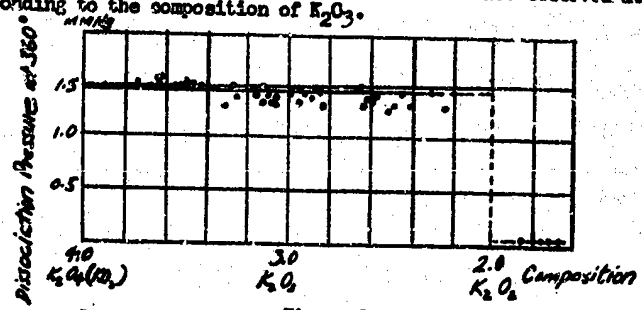


Figure 3

In Table 4 and Figure 3 is presented a summary of the measurements of dissociation pressure of potassium dioxide and products of its thermal disintegration at 360 degrees (for convenience of presentation, we used the formula K_2O_4 in the tables and graphs).

It is seen from the data of Table 4 that in passing from the composition of K_2O_4 to K_2O_2 the dissociation pressure remains practically constant. The average value is 1.45 ±0.1 mm Hg. With a composition lower than K_2O_2 a sharp jump is observed, i.e., the pressure falls to 0.05 mm Hg.

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Table 4

Composition	Dissociation Pressure (in mm Hg)	Composition	Dissociation Pressure (in mm Hg)	Composition	Dissociation Pressure (in mm Hg)	Composition	Dissociation Pressure (in mm Hg)
$K_2O_{3.81}$	1.50	$K_2O_{3.43}$	1.50	$K_2O_{2.97}$	1.48	$K_2O_{2.59}$	1.36
$K_2O_{3.73}$	1.53	$K_2O_{3.37}$	1.47	$K_2O_{2.95}$	1.47	$K_2O_{2.58}$	1.40
$K_2O_{3.69}$	1.55	$K_2O_{3.32}$	1.34	$K_2O_{2.94}$	1.35	$K_2O_{2.50}$	1.34
$K_2O_{3.66}$	1.49	$K_2O_{3.27}$	1.50	$K_2O_{2.92}$	1.43	$K_2O_{2.47}$	1.36
$K_2O_{3.63}$	1.53	$K_2O_{3.25}$	1.40	$K_2O_{2.87}$	1.40	$K_2O_{2.44}$	1.43
$K_2O_{3.62}$	1.52	$K_2O_{3.16}$	1.43	$K_2O_{2.85}$	1.47	$K_2O_{2.41}$	1.36
$K_2O_{3.55}$	1.50	$K_2O_{3.12}$	1.50	$K_2O_{2.82}$	1.46	$K_2O_{2.39}$	1.45
$K_2O_{3.53}$	1.50	$K_2O_{3.10}$	1.38	$K_2O_{2.81}$	1.34	$K_2O_{2.24}$	1.35
$K_2O_{3.32}$	1.50	$K_2O_{3.09}$	1.42	$K_2O_{2.67}$	1.47	$K_2O_{1.86}$	0.05
$K_2O_{3.50}$	1.52	$K_2O_{3.07}$	1.37	$K_2O_{2.66}$	1.50	$K_2O_{1.77}$	0.05
$K_2O_{3.49}$	1.50	$K_2O_{3.06}$	1.40	$K_2O_{2.63}$	1.36	$K_2O_{1.75}$	0.05
$K_2O_{3.48}$	1.49	$K_2O_{3.05}$	1.36	$K_2O_{2.62}$	1.40	$K_2O_{1.79}$	0.05
$K_2O_{3.47}$	1.51	$K_2O_{2.99}$	1.44				

Curves of the dependence of dissociation pressure upon the composition at 370 and 300 degrees show an analogous course (Figures 4 and 5).

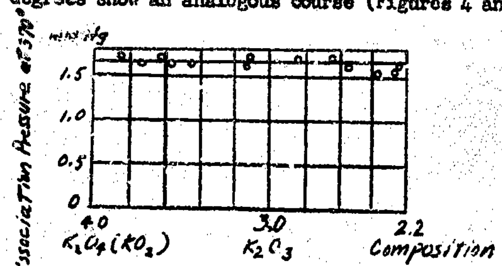

Figure 4

At 370 degrees the dissociation pressure of KO_2 is $1.65 \pm .1$ mm Hg, and at 300 degrees, 0.35 ± 0.1 mm Hg. The total error in measurements can be evaluated at ~ 0.1 mm Hg. The possible error of the temperature was ± 2 degrees C, which corresponds to the variations of P_{O_2} at ~ 0.1 mm Hg. The reading by the McLeod gage was made with an accuracy up to 0.01 mm.

Thus, it was shown that no intermediate phases are formed in thermal disintegration of potassium dioxide within limits from KO_2 (K_2O_4) to K_2O_2 and in the reverse reactions. From this it followed that the potassium trioxide which is described in literature is not a separate compound, but is a mixture of dioxide and peroxide of potassium.

This result was afterwards confirmed by the roentgenographic research of Helms and Klemm (16). Preparations of a composition close to K_2O_3 which they obtained by oxidation of potassium oxide with oxygen gave only roentgenograms of K_2O_2 and KO_2.

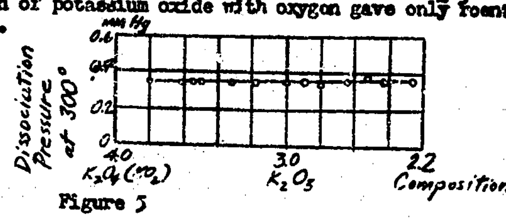

Figure 5

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Determination of Density and Refraction

Until now there was no data on the density of K_2O_2 and on the refraction of K_2O_2 and KO_2. From the refraction of KO_2 the refraction of O_2^- can be established. Apart from this, measurement of the designated magnitude makes it possible to test our deductions on the nature of the so-called potassium trioxide. On the basis of the rule of addition, if our deductions are correct it would be possible to expect an agreement of the molecular volume and the refraction which we found for preparations of composition of K_2O_3 with those for mixtures of KO_2 and K_2O_2 of an analogous composition.

The density was determined pycnometrically in cyclohexane. The temperature of the thermostat was $25 \pm 0.01°$. The values obtained are presented in Table 5.

Table 5

Oxide	Density d_4^{25}	Molecular Volume
KO_2	2.158 ± 0.001	32.95
K_2O_2	2.180 ± 0.001	50.5
(K_2O_3)	2.136 ± 0.003	58.9
$1/2\ (2KO_2 + K_2O_2)$	—	58.2

Table 6

Oxide	Index of Refraction	Molecular Refraction of R
KO_2	1.450	8.85
K_2O_2	1.456	13.58
(K_2O_3)	1.452	15.82
$1/2\ (2KO_2 + K_2O_2)$	—	15.69

The index of refraction was determined with a polarized microscope according to Beck's line by using a mixture of toluene with cyclohexane. The values which were found are presented in Table 6.

The molecular volume (58.9) and refractions (15.82) which were found for potassium trioxide agrees within the limits of possible errors with the calculations for a mixture of $2KO_2 + K_2O_2$ (molecular volume = 58.2; R = 15.69).

Thus the measurement of the density and refraction of preparations of the composition of K_2O_3 do not disagree with the deduction made from the measurement of dissociation pressure.

Table 7

R_{O_2}	$R_{O_2^-}$	$R_{O_2^{--}}$
4.09 [24]	6.60	10.8

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Values of refraction of various molecular ions of oxygen are presented in Table 7. On the basis of the rule of addition, $R_{O_2^-} = R_{KO} - R_{K^+} = 8.85 - 2.25 = 6.60$.

The value of $R_{O_2^{=}}$ was calculated from earlier measurement of the refraction of barium peroxides (20).

According to its polarizability the ion O_2^- occupies a place between the ions F^- ($R_{F^-} = 2.44$) and Cl^- ($R_{Cl^-} = 9.07$). The ion $O_2^{=}$ has somewhat greater polarizability than the ion of chlorine (crystals of KO_2 and BaO_2, in relation to the tetragonal system, have two indices of refraction (ω and ε) and for calculation of molecular refraction with the Lawrence-Lawrence equation, it would be necessary to substitute $\eta = \sqrt[3]{\omega^2 \varepsilon}$).

<u>Thermochemistry of Potassium Oxides</u>

In the textbook on thermochemistry of Bichowskiy and Rossini (22), the following measurements of the heat of formations (Qf) of oxides of potassium are presented:

$2K + \frac{1}{2}O_2 = K_2O$; $Qf(K_2O) = 86.2$ kcal (Rengade, 1907 [23])

$2K + \frac{3}{2}O_2 = K_2O_3$; $Qf(K_2O_3) = 126.0$ kcal (Forcrand, 1914 [14])

$2K + 2O_2 = K_2O_4$; $Qf(K_2O_4) = 135.0$ kcal (Forcrand, 1914 [14])

It is shown in the present work that potassium trioxide is a mixture of two moles of KO_2 and one mole of K_2O_2. Thus Forcrand's measurement can be used to determine the heat of formation of K_2O_2, which was unknown until now. We have $Qf(K_2O_3) = Qf(KO_2) + \frac{1}{2}Qf(K_2O_2)$

and $$Qf(K_2O_2) = 2[Qf(K_2O_3) - Qf(KO_2)].$$

Substituting the value of $Qf(K_2O_3) = 126$ kcal and $Qf(KO_2) = 67.5$ kcal, we get $QF(K_2O_2) = 117$ kcal.

For the reaction

$$K_2O + \frac{1}{2}O_2 = K_2O_2$$

we find

$$Q_1 = 117.0 - 86.2 = 30.8 \text{ kcal}.$$

For the reaction

$$K_2O_2 + O_2 = 2KO_2$$

we have

$$Q_2 = 135.0 - 117.0 = 18.0 \text{ kcal}.$$

Similarly, the heating effect of this reaction can be determined approximately from our measurement of dissociation pressure of KO_2.

If $\frac{1}{T}$ is laid out along the abscissa and $\log P_{O_2}$ along the ordinate axis, then the measured values of P_2 lie on a straight line, the equation of which is

$$\log P_{O_2} = -\frac{3411}{T} + 2.654.$$

It follows from Table 8 that the calculated dissociation pressures satisfactorily agree with the measured pressures.

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We get

$$Q = -\Delta H = 4.574 \cdot 3411 = 15.6 \text{ kcal}$$

for the heat effect of reaction (3) by a comparison with the thermodynamic equation

$$-\log P_O = -\frac{\Delta H}{4.574T} \quad \frac{\Delta S^o}{4.574}.$$

Table 8

t^oC	P_{O_2} (in mm Hg) Measured	Calculated
300	0.35	0.40
360	1.45	1.40
370	1.65	1.75

The magnitude of ΔC_p for a given reaction is

$$\Delta C_p = 2C_p(KO_2)[24] - C_p(K_2O_2)[25] - C_p(O_2) = 2 \cdot 19.6 - 22.8 - 1.7 = 9.3 \text{ cal/degrees}$$

From this we find the heat effect at room temperature

$$Q_{298} = Q_{603} + (603 - 298)\ 9.3 \cdot 0.001 = 15.6 + 2.8 = 18.4 \text{ kcal}.$$

For the heat of formation of K_2O_2, we have

$$Qf(K_2O_2) = 2Qf(KO_2) - 18.4 = 135.0 - 18.4 = 116.6 \text{ kcal},$$

which is in satisfactory agreement with the value of 117 kcal, obtained above in Forcrand's new treatise on thermal measurement.

In conclusion, we present a summary of the thermal data for potassium oxides (Table 9).

Table 9

Oxide	Heat of Formation from the Elements, (in kcal)	Heat of Reaction of Addition of Oxygen
K_2O	86.2	
K_2O_2	117.0	$K_2O + 1/2O_2 = K_2O_2 + 30.8$ kcal
KO_2	67.5	$K_2O_2 + O_2 = 2KO_2 + 18.0$ kcal

From the data of Table 9, it is seen that Forcrand's empirical law remains in force. This law states that the thermal effect on one atom of oxygen decreases according to the measure of further additions of oxygen to the oxides of alkali metals.

The theoretical explanation of this regularity is given by Kazarnovskiy in another work (26).

RESULTS

1. Some properties of the oxides KO_2, RbO_2, CsO_2 and the molecular ion of oxygen O_2^- were examined.

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2. It is shown that the arguments presented by the various authors supporting the existence of potassium trioxide are not conclusive.

3. The tensimetric research which is presented in the present work shows that no intermediate phases are formed in thermal disintegration of potassium dioxide in the limits from KO_2 (K_2O_4) to K_2O_2 and in reverse reaction. Consequently, the potassium trioxide which is described by many authors is not a separate compound, but is a mixture of dioxide and peroxide of potassium.

4. The density and refraction of K_2O_2 and KO_2 were measured. The value of 6.60 was found for the refraction of the ion O_2^-. Study of the density and refraction of preparations of the composition of K_2O_3, which were obtained by thermal disintegration of potassium dioxide, gave values corresponding to those for a mixture $2KO_2 + K_2O_2$.

5. Consequently, there are three oxides of potassium: potassium oxide, K_2O; potassium peroxide, K_2O_2; and potassium dioxide, KO_2.

6. On the basis of Forcrand's calorimetric measurements and data of the present work, the thermochemistry of potassium oxides are examined. The heat of formation of K_2O_2 was found as 117.0 kcal, which was unknown until now.

This value agrees with the value calculated from our measurements of the dissociation pressure, 116.6 kcal.

NOTE

Previous works of the laboratory of inorganic peroxides:

I. I. A. Kazarnovskiy, Zhurn. Fiz. Khim. I, 93, 1930: "The Structure of Inorganic Peroxides" (hydrogen peroxide).

II. S. I. Raykhshteyn and I. A. Kazarnovskiy, Zhurn. Fiz. Khim. III, 83, 1932: "The Structure of Inorganic Peroxides," 2d article barium peroxide.

III. J. D. Bernal, E. Djatlowa, I. Kasarnovskiy, S. Raykhshteyn, A. Ward, Z. Kristallogr. ogr., 92, 344, 1935 (Structure SrO_2 and BaO_2).

IV. V. Kasatochkin and V. Kotov, Zhurn. Fiz. Khim. VIII, 620, 1936; Journ. Chem. Phys. 4, 458, 1936: "Structure of Potassium Tetraoxide."

V. S. I. Raykhshteyn and I. A. Kazarnovskiy, Zhurn. Fiz. Khim. XI, 743, 1938: "Does Potassium Trioxide Exist?"

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VII. V. Kotov and S. Raykhshtey, Zhurn. Fiz. Khim. XV, 1057, 1941: "The Structure of Peroxide CaO_2."

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IX. I. A. Kazarnovskiy, "Theory of Formation of Peroxides and Their Structure" (in publication).

X. S. I. Raykhshteyn and I. A. Kazarnovskiy, "Apparatus for Determining Dissociation Pressure," Zhurn. Fiz. Khim. XXI, 257, 1947.

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